ADVANCED REACTOR SAFEGUARDS

Process monitoring for MC&A: Optical spectroscopy

PNNL-SA-172291

PRESENTED BY

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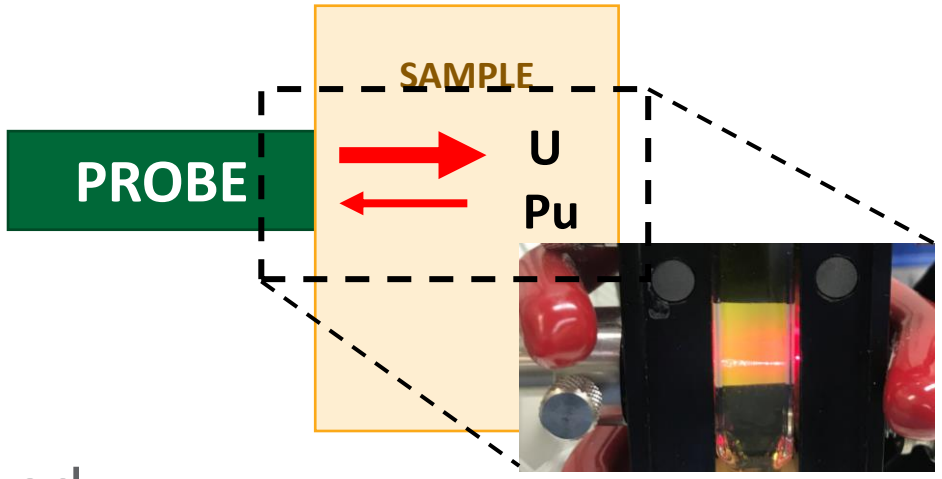
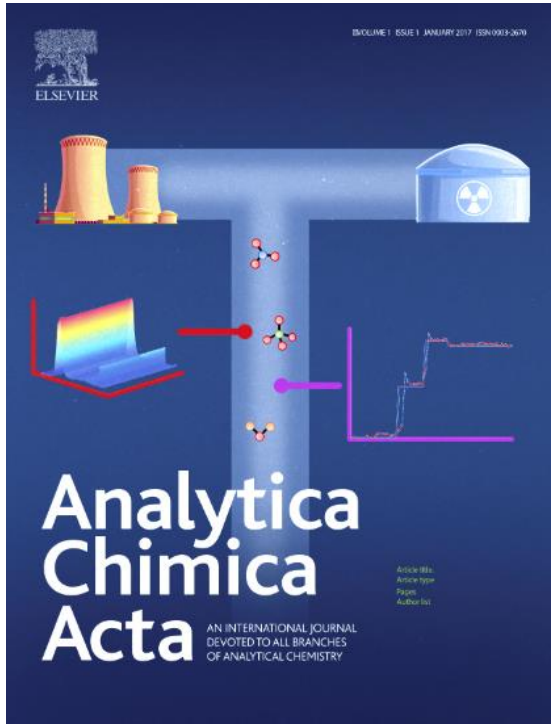
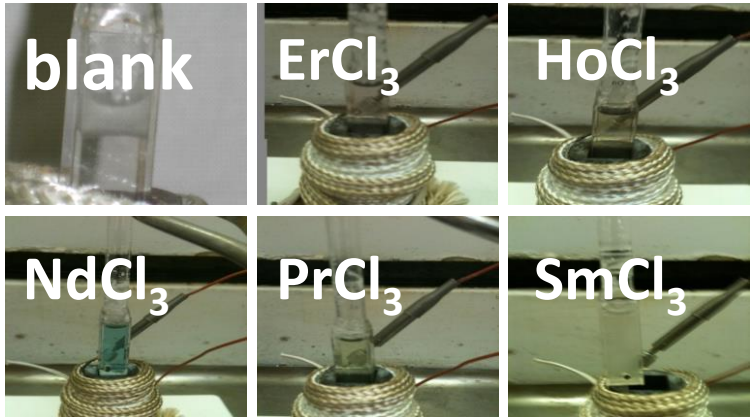
Sandia National Laboratories | U.S. DEPARTMENT OF ENERGY

Common Process Monitoring Goals in Industry

- Fundamental characterization
- Design phase
  - Informed and optimized R&D
- Deployment phase
  - Process optimization
  - Process control
  - Material accounting



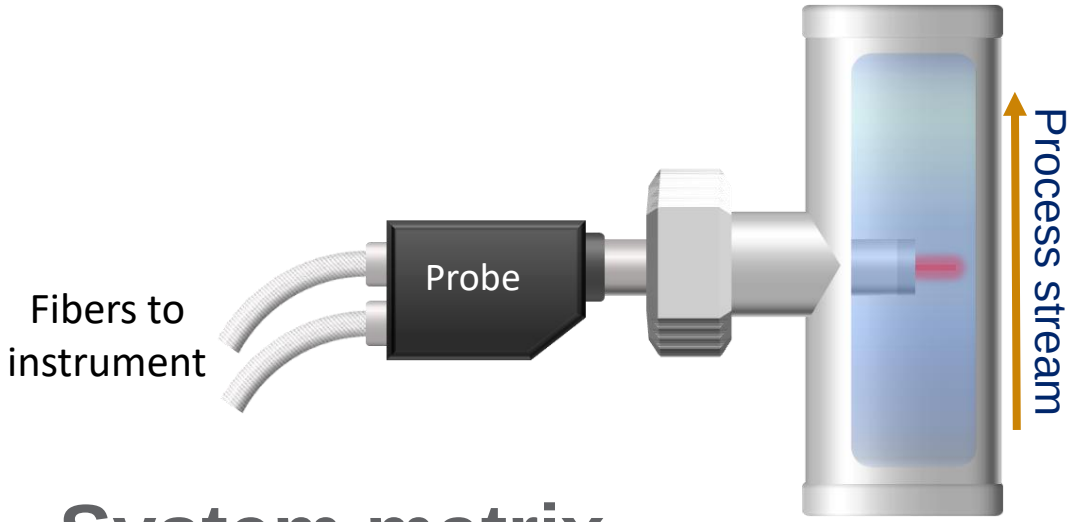




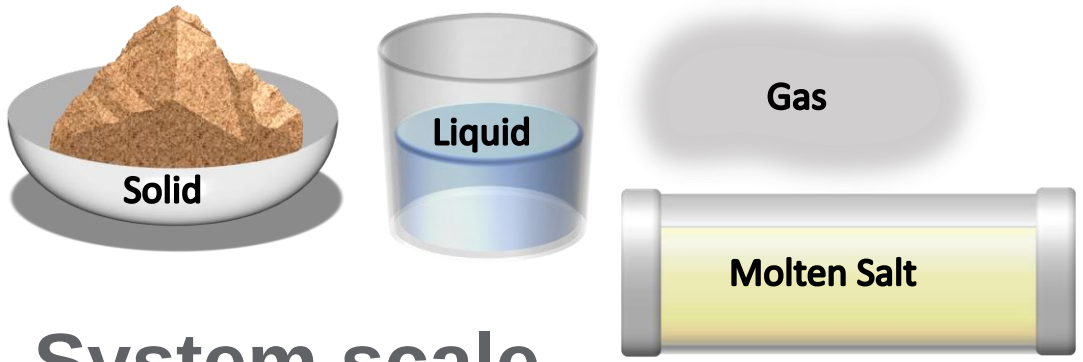
Tse, P., N.P. Bessen, S.A. Bryan, A. M. Lines, J.C. Shafer. "Review of On-line and Near Real Time Spectroscopic Monitoring of Processes Relevant to Nuclear Material Management" ***Analytica Chimica Acta***, 2020, 1107:1-13,

Chemical Characterization: Optical Spectroscopy

- Provides chemical information
  - Identification and quantification
  - Oxidation State
    - ✓ Essential information for control of systems
  - Molecular and elemental species
    - ✓ Essential information to control general system behavior (e.g., precipitation, species interaction)
- Highly mature technology
- Simplistic integration
- Versatile



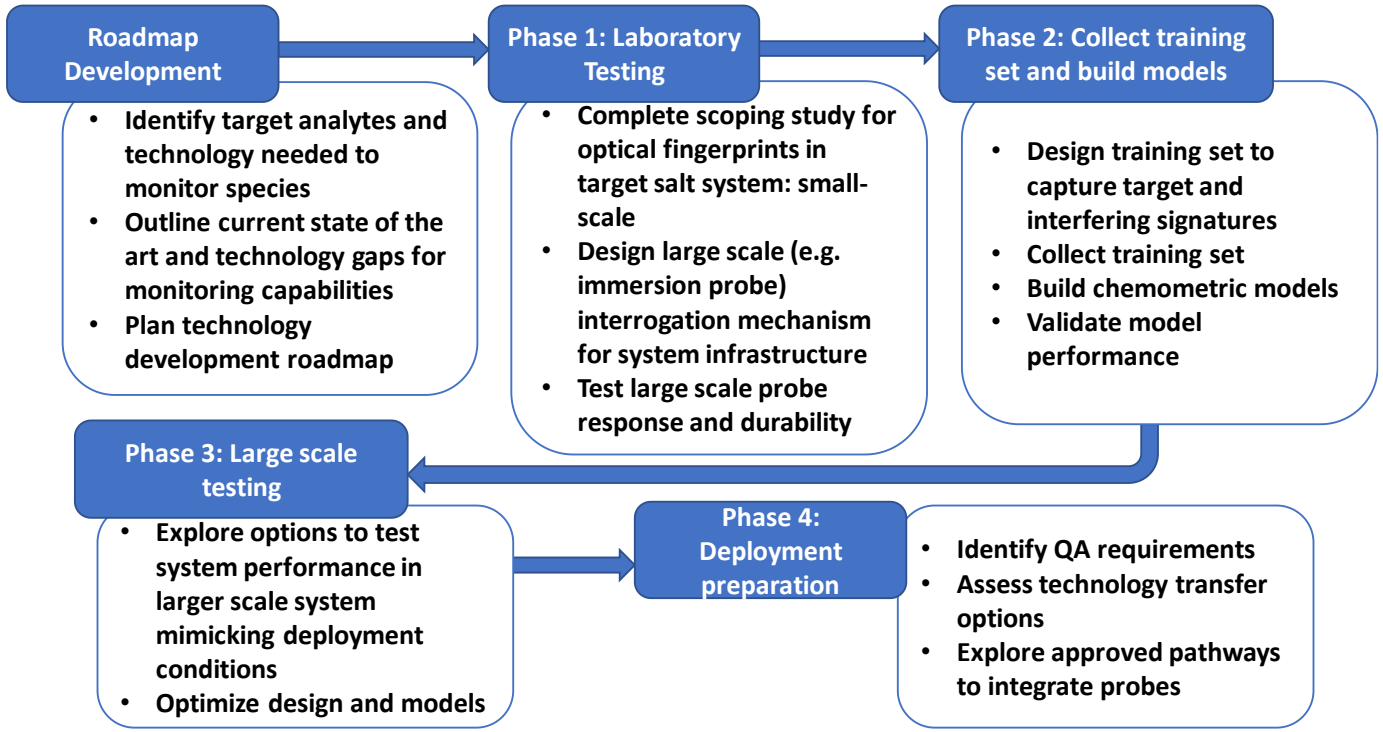
System matrix



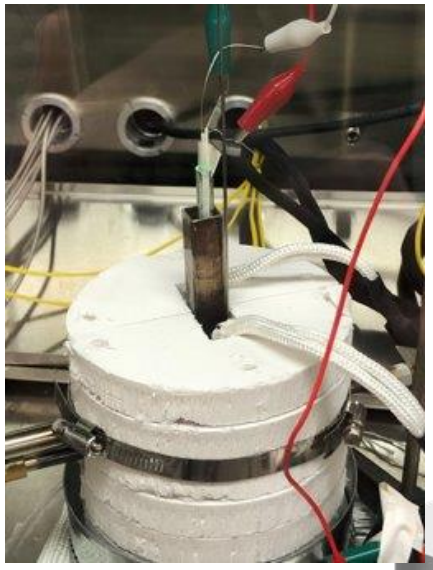
System scale

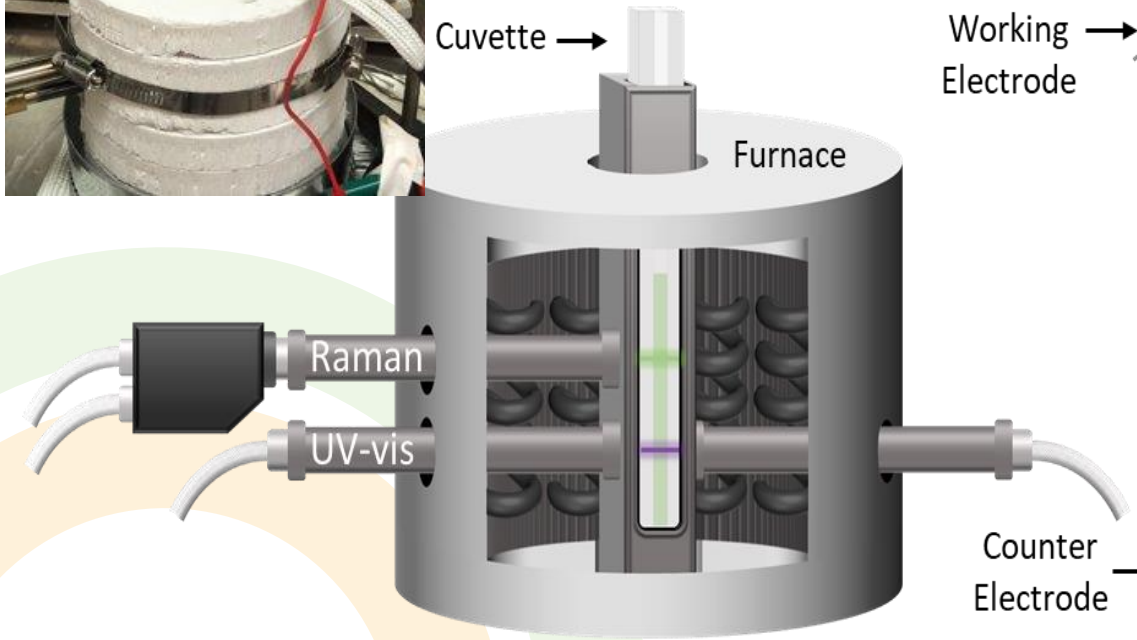
Applications to MC&A in MSRs

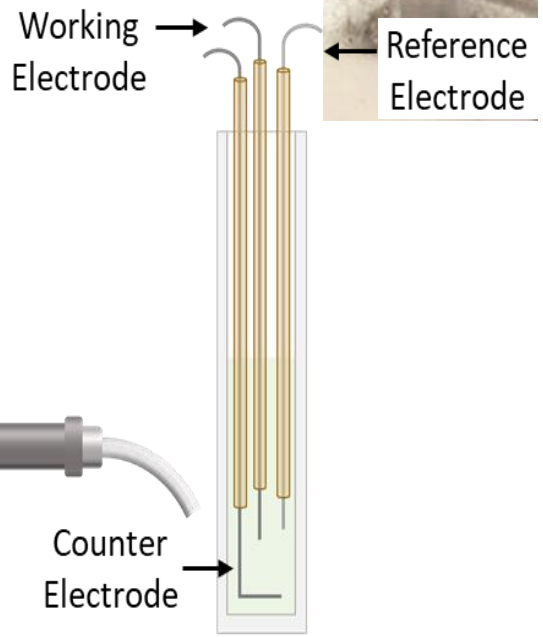
- MSR systems pose unique challenges to MC&A analysis
- Building robust capabilities for in-line analysis of the system could provide needed information without opening the system for grab sample collection
- **Provide needed information and measurement uncertainty for actinides and other key targets without placing undue burden on the MSR system**



PNNL Capabilities: FY21 Accomplishments







FY22 Goals and Progress Overview

- M2RS-22PN0401051: Determine Feasibility of Optical Spectroscopy for Actinide Quantification in MSRs (9/30/2022, on time)

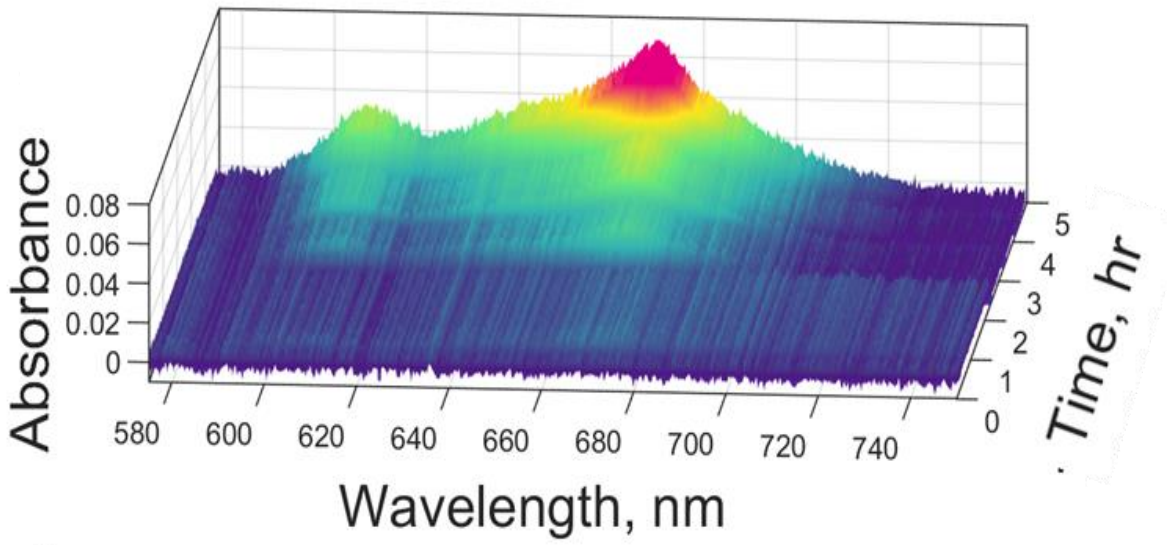
- Collection of optical data (training and validation sets)
  - Opportunity to partner with Industry (e.g., TerraPower) to look at representative salts
- Building chemometric models for accurate/automated data analysis
- Determining uncertainties, limits of detection, etc and comparing to MC&A needs/requirements

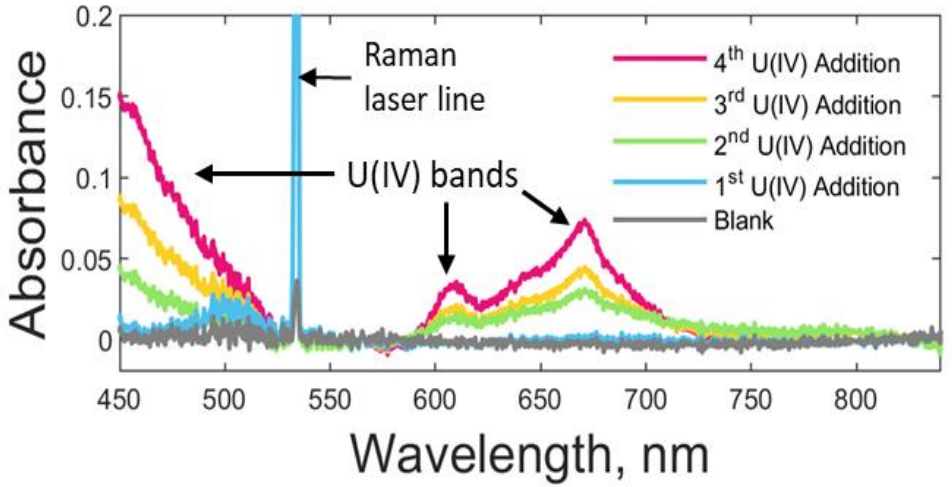
Collection of Optical Data: Overview

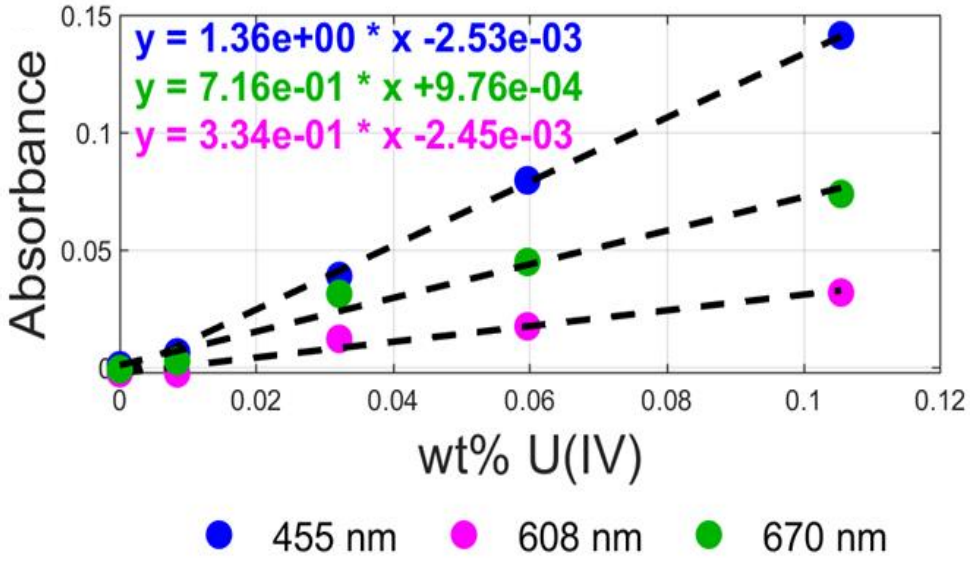
- Optical spectroscopy can provide the complete inventory (e.g. total U) but can also provide needed insight into chemical complexity of process
  - Indicators of precipitation or interaction that could impact accounting

- Cl based melts
  - Fingerprints will be slightly different in F, but approach is the same
- Exploring multiple salt types/temperatures to gain insight into flexibility of application
  - But heavily taking advantage of opportunity to characterize representative salts provided by industry partner

Collection of Optical data: U(IV) in NaKMg-Cl



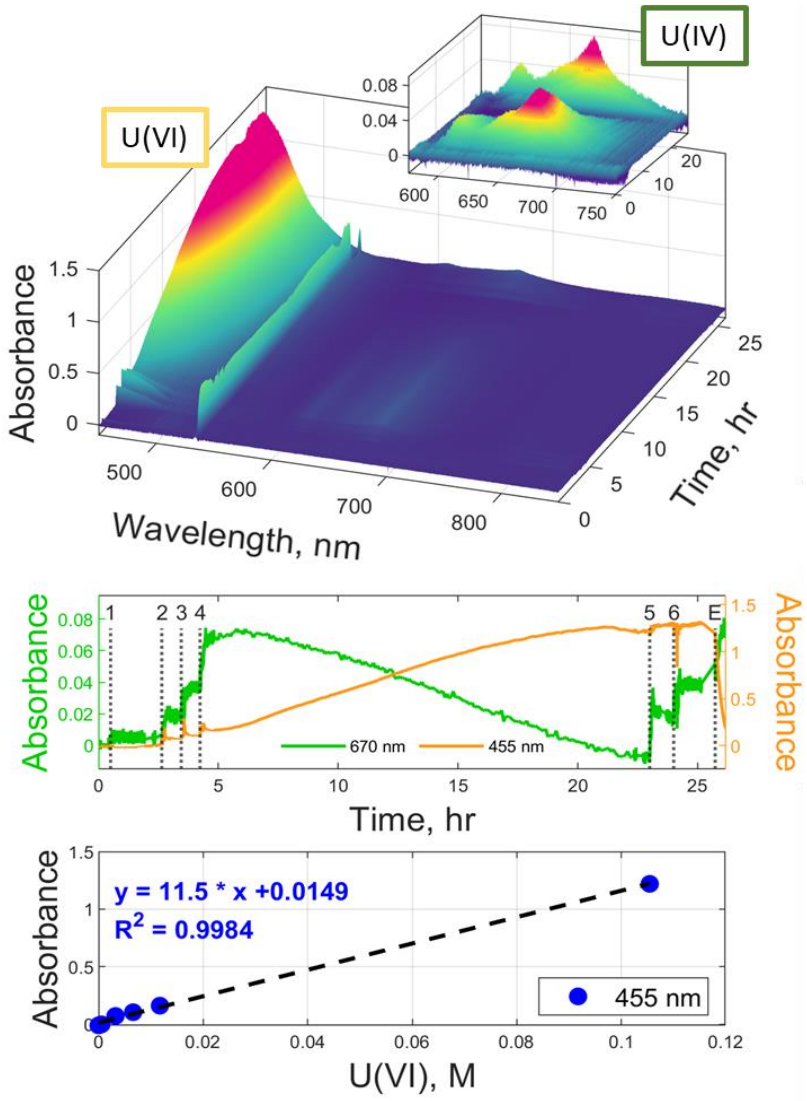




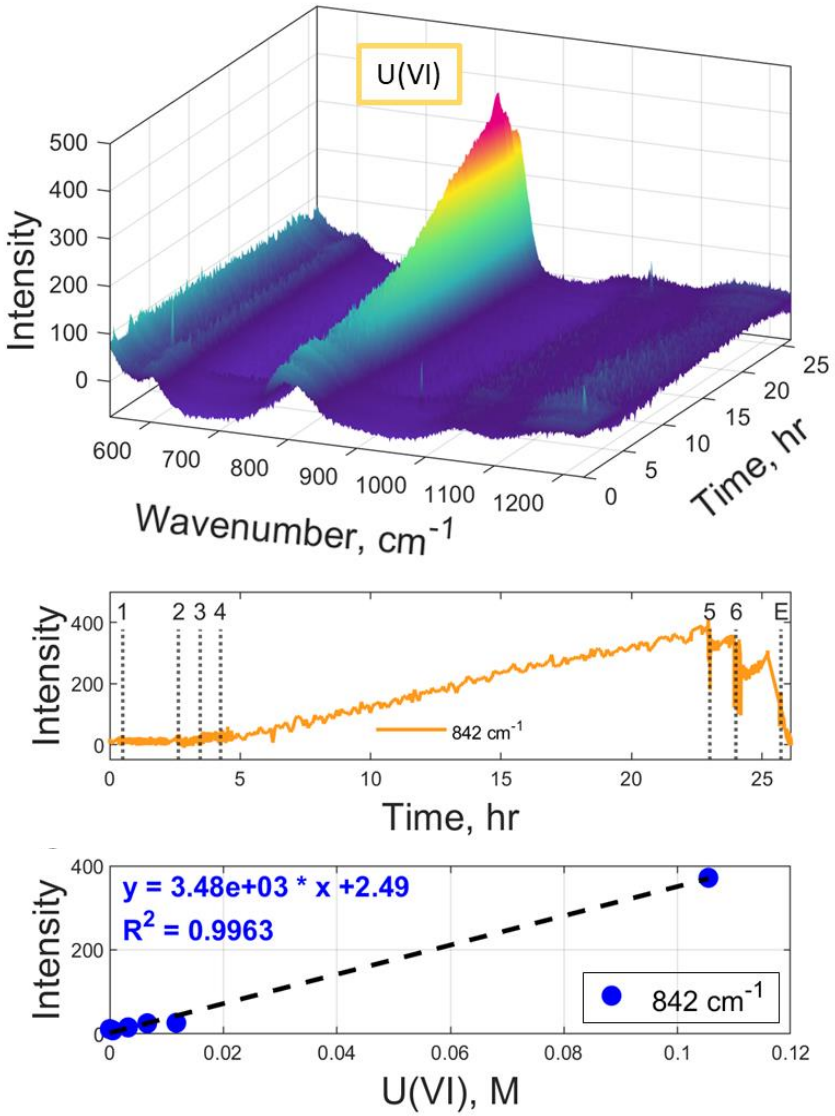
Collection of Optical data: U(VI) in NaKMg-Cl

Real-time monitoring of conversion from U(IV) to U(VI)

UV-vis

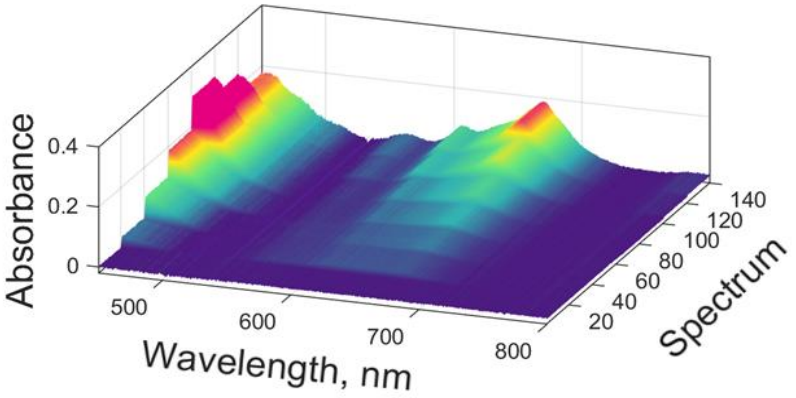


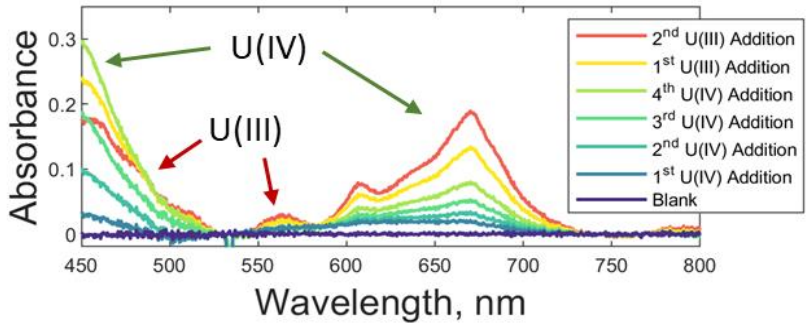
Raman

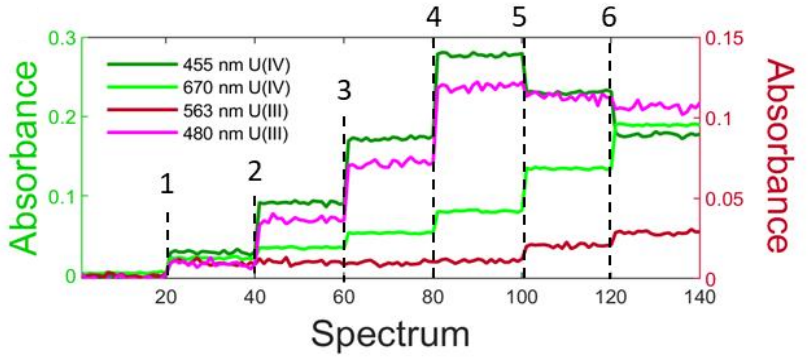


Collection of Optical data: U(IV) and U(III) in LiK-Cl

- Following cleaning of salt
  - Sparging with HCl under vacuum for 6 hrs
- Prior to cleaning impurities from LiCl (purchased as 99.9% anhydrous) caused U to very quickly oxidize



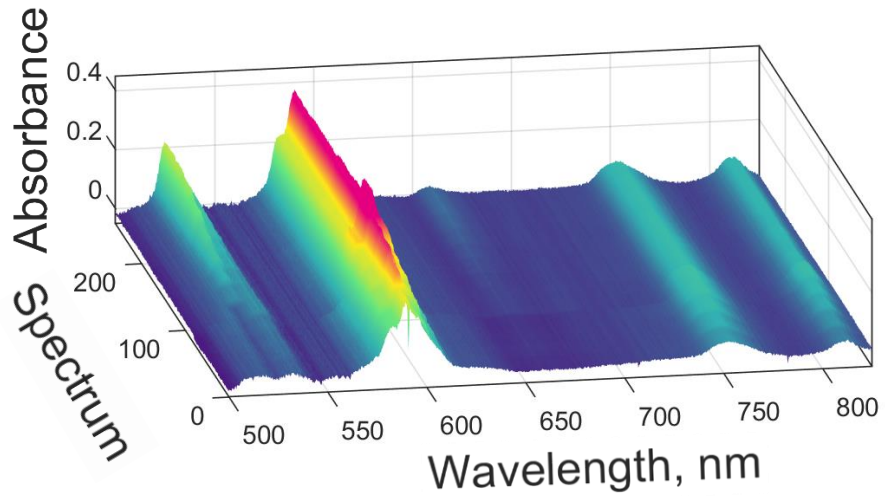


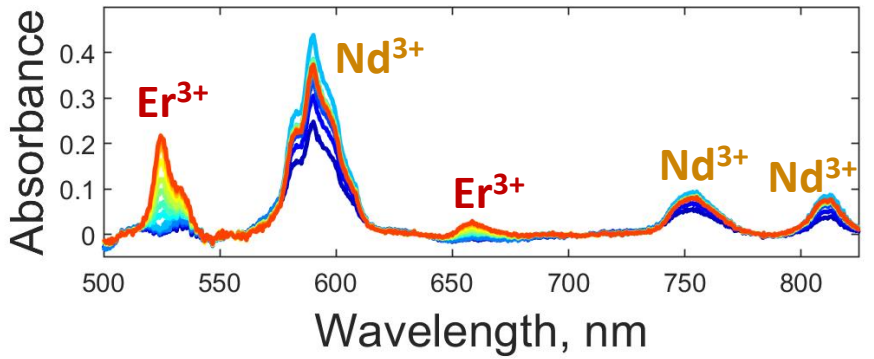


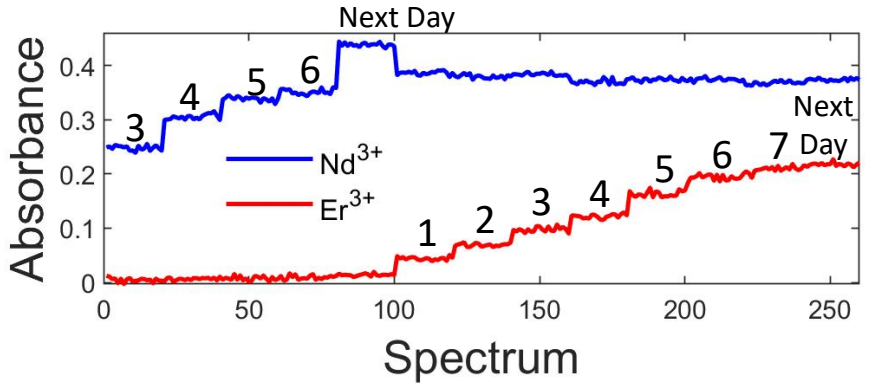
Complex chemistry: Addition of fission products

- Ability to track unique fingerprints in presence of interfering species

Nd^{3+} Nd^{3+} + Er^{3+}

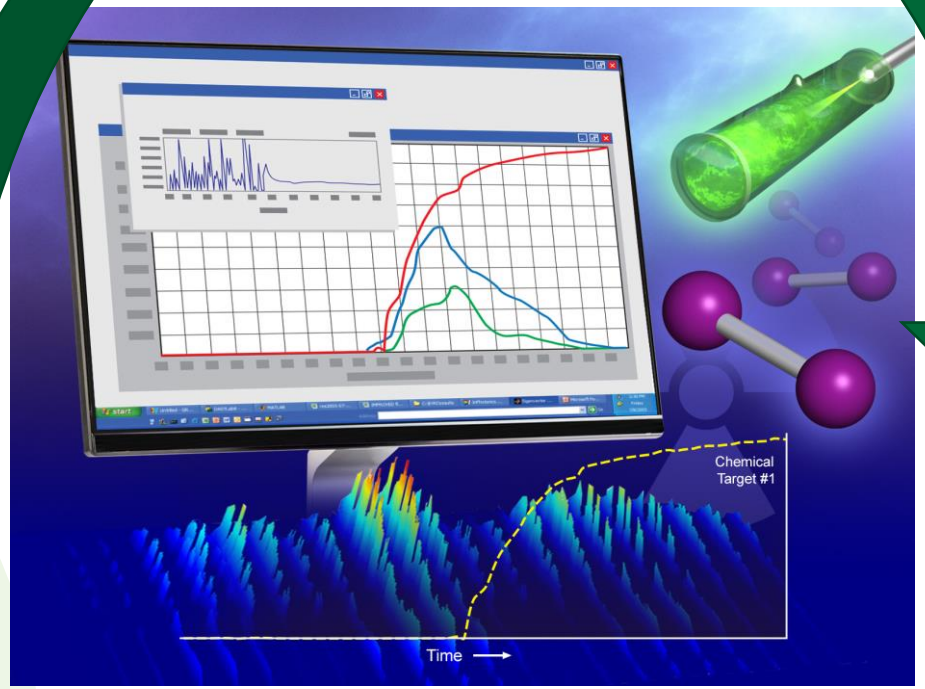






Chemometric Model Building

Data

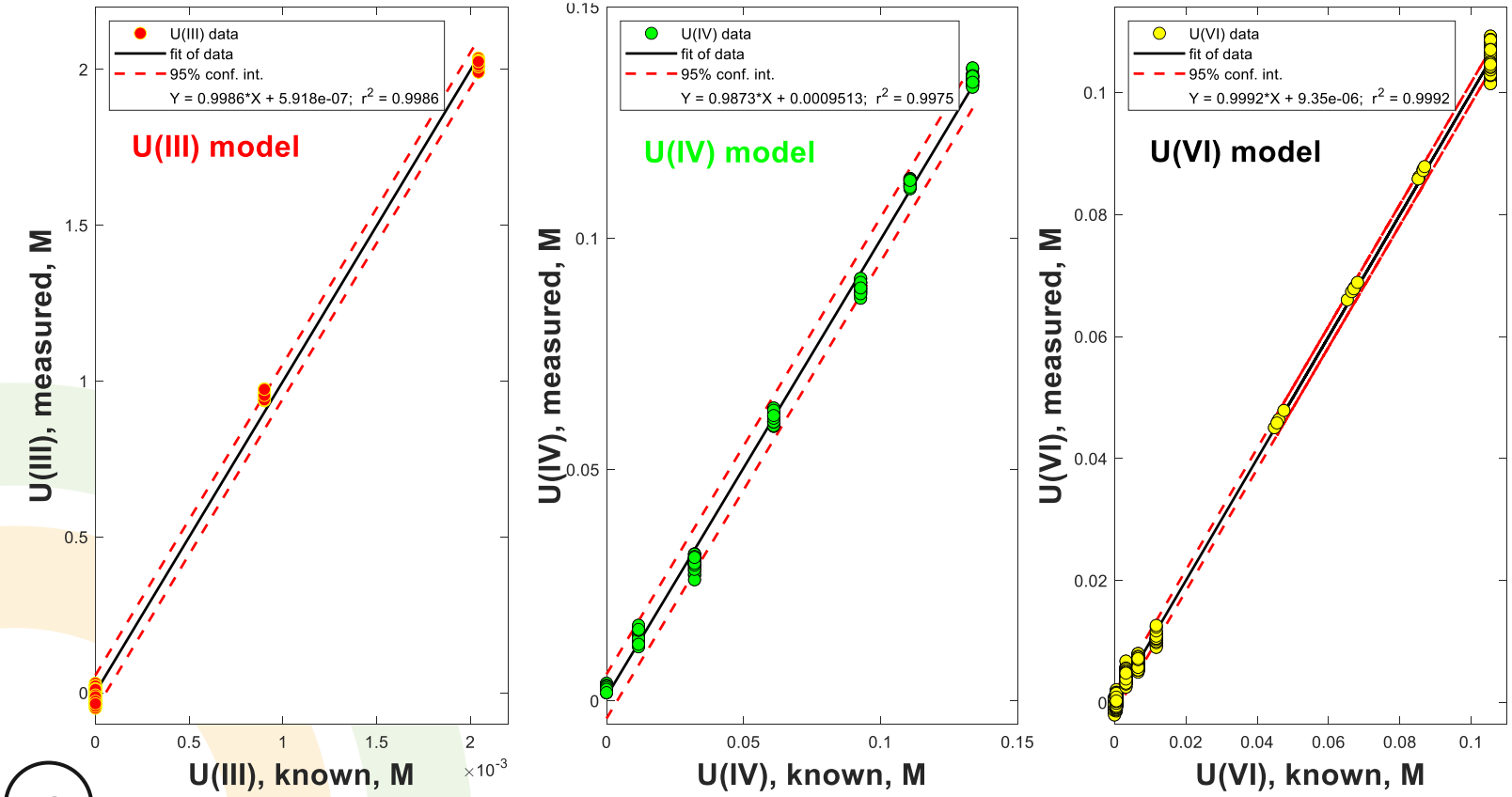


Enabling researchers and operators to understand complex processes with *in situ* and real-time feedback on process conditions

Information

Chemometric Model Building

- Initial chemometric model showing accurate analysis of U in both (IV) and (VI) oxidation states within molten salt environment

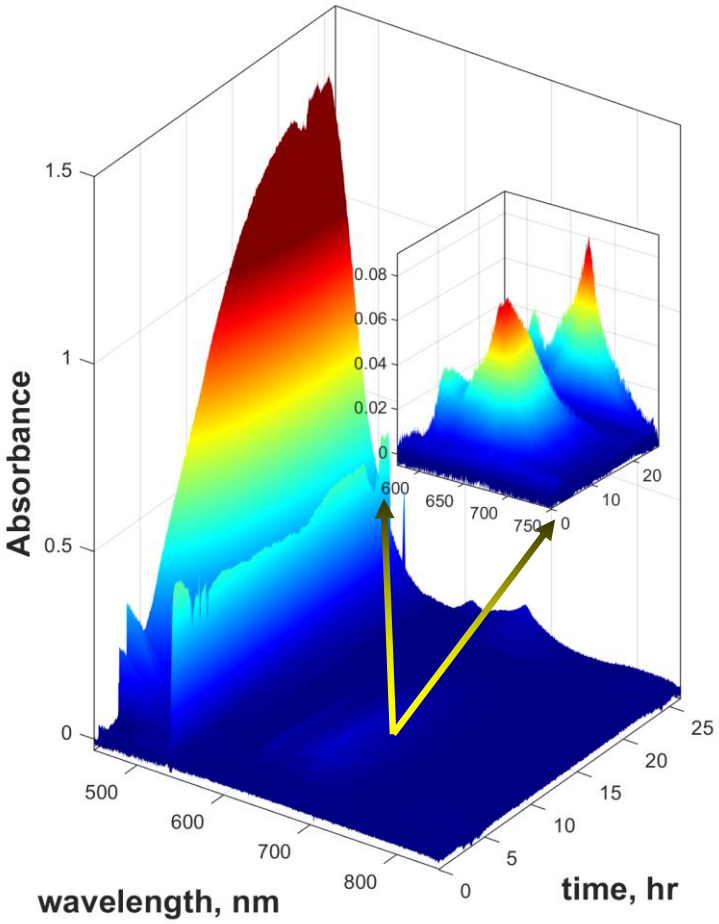


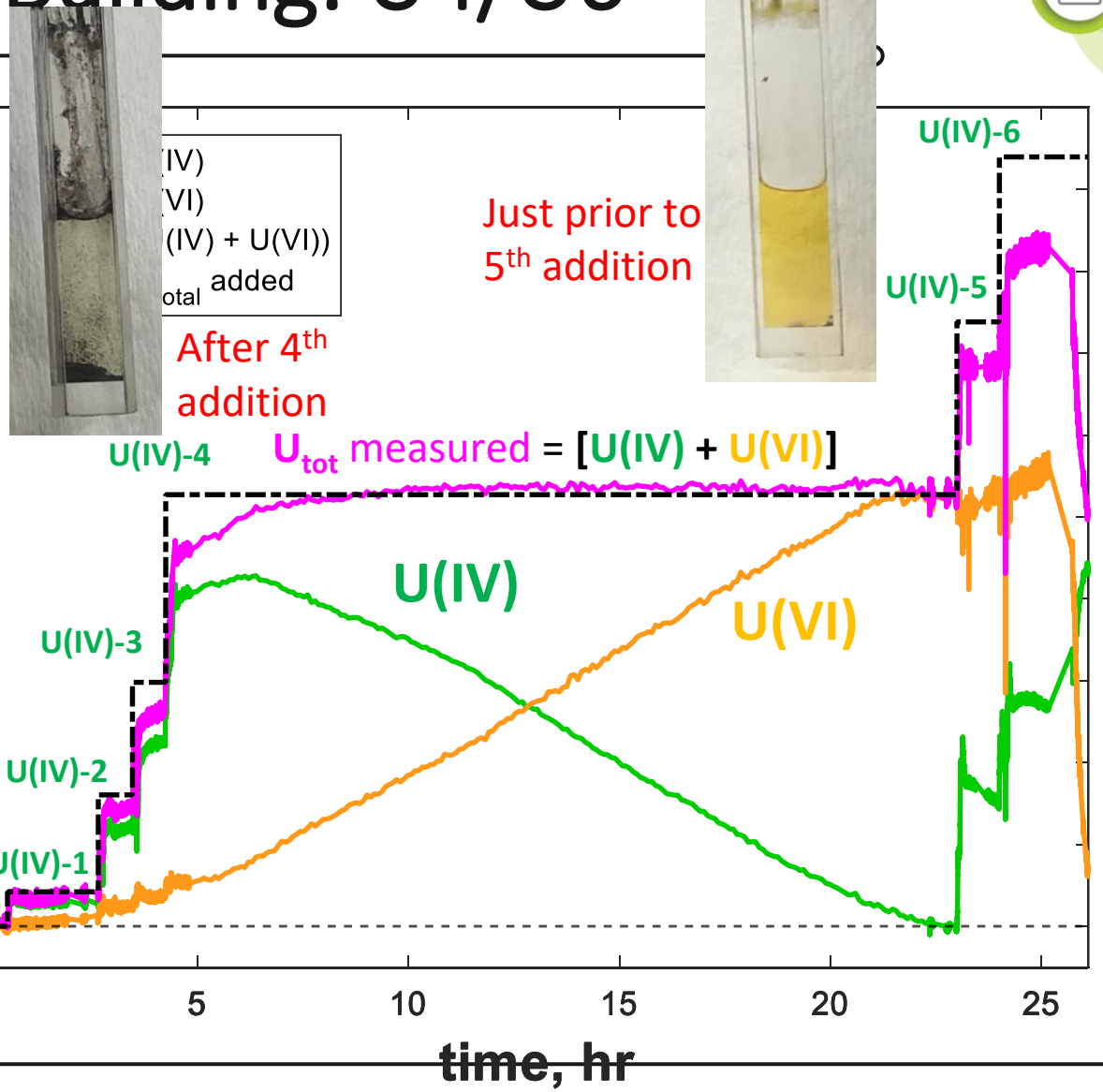
RMSECV (uncertainty)

U(IV) 0.0014 M
U(VI) 0.0011 M

Continuing to optimize models

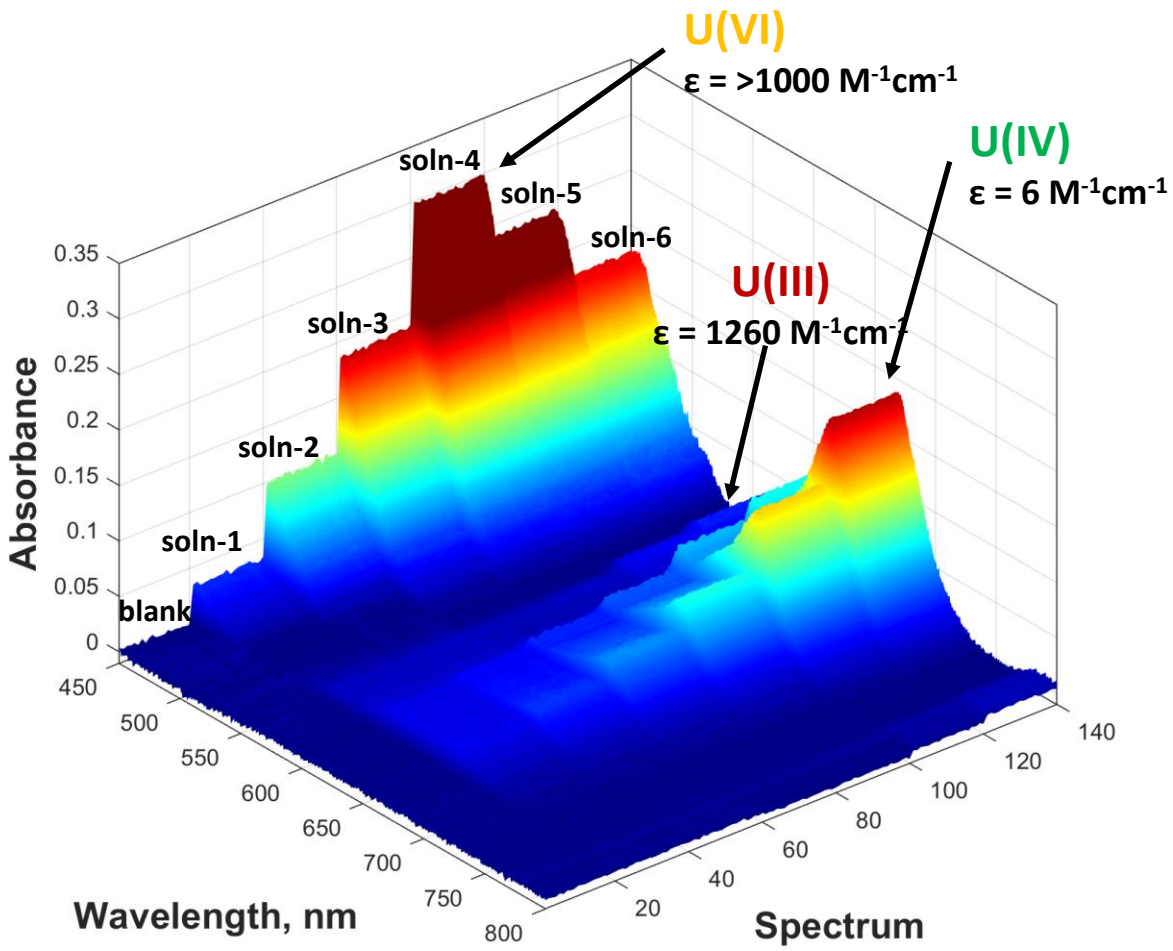
Chemometric Model Building: U4/U6

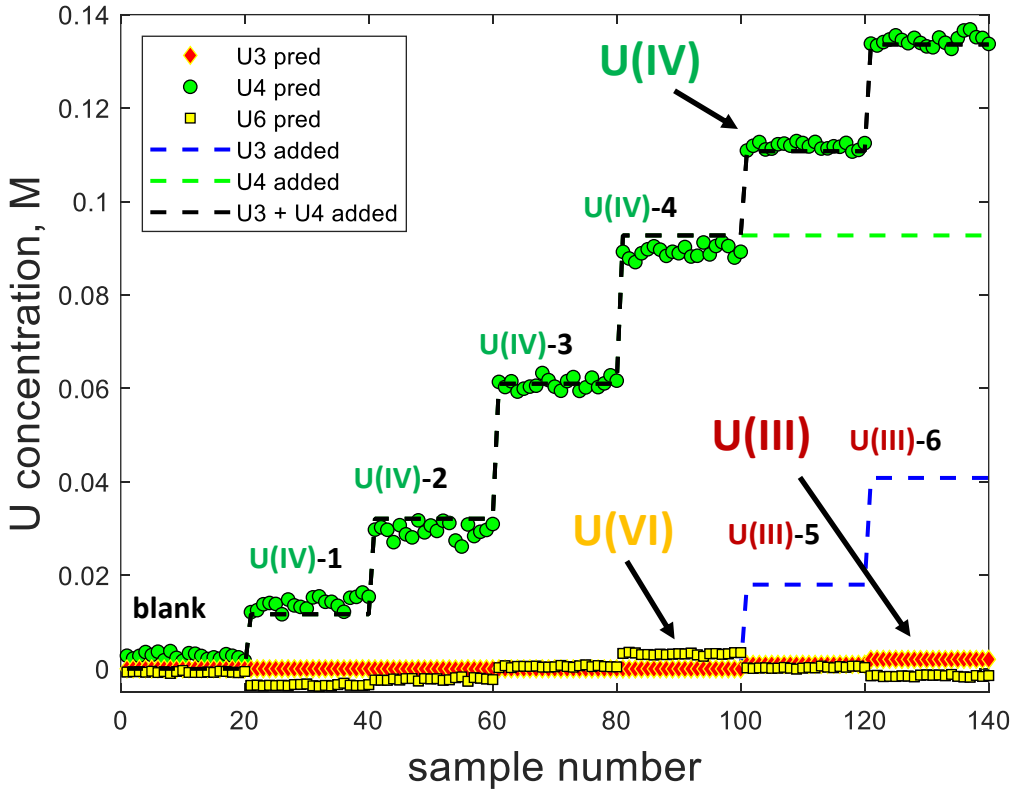




Chemometric Model Building: U3/U4/U6

Soln-ID	U-added
blank	-----
Soln-1	U(IV)
Soln-2	U(IV)
Soln-3	U(IV)
Soln-4	U(IV)
Soln-5	U(III)
Soln-6	U(III)

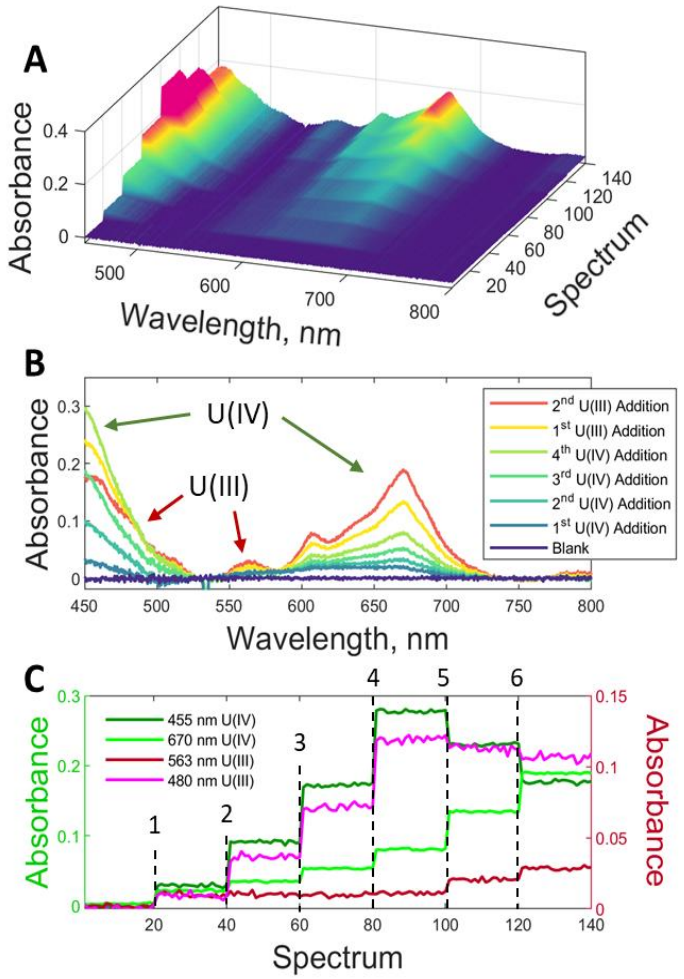




Nagai, T., et al. (2005). **Journal of Nuclear Science and Technology** 42(12): 1025-1031; Nagai, T., et al. (2004). **Journal of Nuclear Science and Technology** 41(6): 690-695.

Next steps

- Concluding data set collection
  - Much of the needed sets are complete but we will continue to take advantage of opportunities to look at industry or other relevant salts
- Chemometric modeling
  - Characterize uncertainty, limits, and working ranges
- Determine if optical spectroscopy can meet MC&A needs



Acknowledgements

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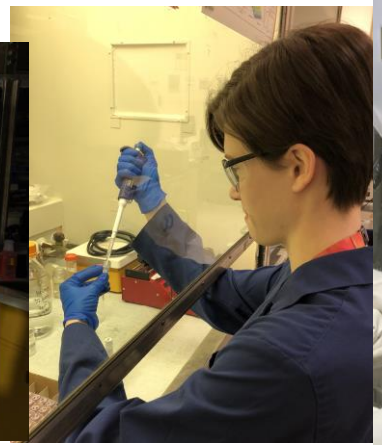
Andrew Clifford

U.S. DOE NE, ARS campaign










Thank you